($C_{65}H_{67}Cl_2N_3O_2P_4Pd_2S\cdot CH_2Cl_2$): $M_r = 1446.78$, yellow prism, triclinic, space group $P\bar{1}$, $a = 13.311(2)$, $b = 14.002(1)$, $c = 19.661(3)$ Å, $\alpha = 95.07(1)$, $\beta = 106.45(2)$, $\gamma = 105.35(1)^\circ$, $V = 3335.8(8)$ Å^3, $Z = 2$. **4** ($C_{65}H_{67}Cl_2NO_2P_4Pd_2S\cdot CH_2Cl_2$): $M_r = 1418.76$, red prism, monoclinic, space group $P2_1/c$, $a = 19.037(1)$, $b = 15.689(1)$, $c = 21.576(2)$ Å, $\beta = 97.92(1)^\circ$, $V = 6382.7(8)$ Å^3, $Z = 4$.

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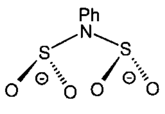
Formation of the Azadisulfite Dianion $[O_2S(\mu\text{-NPh})SO_2]^{2-}$ by Twelvefold Insertion of SO_2 into the Mg–N(Ph) Bonds of $[(thf)MgNPh]_6$**

Justin K. Brask, Tristram Chivers,* and Masood Parvez

The insertion of a sulfur dioxide molecule into a metal–carbon σ bond is a widely studied reaction.[1a] For example, SO_2 reacts with organomagnesium reagents to give, upon hydrolysis, sulfinic acids.[1a, 2] The facile insertion of SO_2 into the M–O bonds of the polymeric metal alkoxides $[M(OMe)_2]_n$ (M = Ca, Mg) yields the corresponding methylsulfites.[3] Sulfur dioxide also undergoes insertion into M–NR_2 linkages (e.g., Me_3SnNMe_2).[4] Despite the recent interest in both transition metal[5] and main group imido chemistry,[6–8] the reaction of SO_2 with an "MNR" group has not been reported. Divalent main group imides are normally oligomers, for example the hexagonal prism $[(thf)MgNPh]_6$,[6a] and the outcome of the reaction of these clusters with SO_2 is not readily predictable. Here we describe the generation of the novel azadisulfite anion $[O_2S(\mu\text{-NPh})SO_2]^{2-}$ (**1**) by the reaction of SO_2 with $[(thf)MgNPh]_6$. To our knowledge this is the first report of the double insertion of SO_2 into a single functional group. We also describe the product of the reaction of $[(thf)MgNPh]_6$ with *t*BuNSO, in which the $[(thf)_2MgNPh]_2$ dimer is trapped by cycloaddition with two molecules of *t*BuNSO.



1

When SO_2 gas is bubbled into a slurry of $[(thf)MgNPh]_6$[6a] in THF, an immediate reaction occurs to give a yellow solution and, subsequently, a pale yellow precipitate. The product **2** is insoluble in diethyl ether, *n*-hexane, and *n*-pentane, sparingly soluble in THF and toluene, but soluble in benzene. Elemental analyses and $^1H/^{13}C$ NMR spectra of **2** are consistent with the retention of the 1:1 ratio of THF:Ph ligands and the uptake of two SO_2 molecules per MgNPh unit. The X-ray crystal structure analysis[9] of **2** confirmed these conclusions and revealed that a hexameric arrangement is maintained (Figure 1).

$[(thf)Mg\{O_2S(\mu\text{-NPh})SO_2\}]_6$ **2**

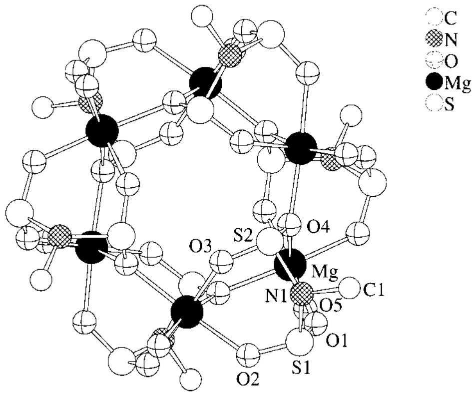


Figure 1. Molecular structure of **2**. For clarity, only the oxygen atoms O5 of the THF molecules and the *ipso*-C atoms of the phenyl groups are shown. Mean values and ranges of bond lengths [Å]: S-O 1.52, 1.479(17)–1.553(16), S-N 1.73, 1.72(2)–1.74(2), Mg-O(λ^2) 2.03, 2.00(2)–2.046(18), Mg-O(λ^3) 2.17, 2.151(18)–2.194(17), Mg-O(THF) 2.068(17).

Complex **2** contains a 48-atom $Mg_6S_{12}N_6O_{24}$ quaternary cluster core with S_6 molecular symmetry. It can be viewed as the result of the insertion of twelve SO_2 molecules into the Mg–NPh bonds of $[(thf)MgNPh]_6$ (Scheme 1), which generates the novel azadisulfite dianion $[O_2S(\mu\text{-NPh})SO_2]^{2-}$ (**1**).[10] Each of these dianions bis-chelates two Mg^{2+} cations, and one oxygen atom exhibits monodentate coordination to a third Mg^{2+} ion. Thus the fundamental building block in the cluster is the adamantane-like $Mg_2S_2O_5N$ unit **3**; each of these units is

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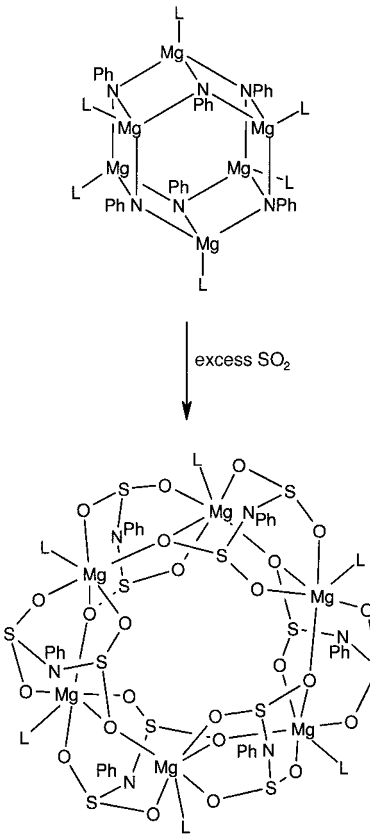
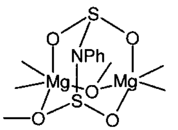


2

Scheme 1. Formation of **2** (L = thf) from [(thf)MgNPh]$_6$.

fused to two neighboring units through shared Mg–O edges.[11] A THF ligand completes the octahedral coordination at each Mg^{2+} ion.



3

For comparison, the reaction of [(thf)MgNPh]$_6$ with the heteroallene *t*BuNSO, which is isoelectronic with SO$_2$, was also investigated. In THF solution this reaction produces the magnesium diazasulfite **4**. The ^{1}H NMR spectrum of **4** in [D$_8$]THF showed signals for *t*Bu, Ph, and THF ligands in the ratio 1:1:2, consistent with the uptake of one *t*BuNSO molecule per MgNPh unit.

[(thf)$_2$Mg{OS(N*t*Bu)(NPh)}]$_2$ **4**

X-ray crystal structure analysis of **4**[12] revealed a dimeric structure in which the (MgNPh)$_2$ dimer (one face of the hexagonal prism in [(thf)MgNPh]$_6$)[6a] is trapped by cycloaddition to two molecules of *t*BuNSO to give the Mg^{2+} salt of the pyramidal diazasulfite dianion [OS(N*t*Bu)(NPh)]$^{2-}$ (Figure 2). Previously reported dilithium diazasulfites [Li$_2${OS(N*t*Bu)(NR)}]$_6$ (R = *t*Bu, SiMe$_3$) form hexameric 36-atom Li$_{12}$S$_6$N$_{12}$O$_6$ clusters.[13] The structure of the centrosymmetric Mg$_2$S$_2$O$_2$N$_4$ cluster core in **4** is reminiscent of the "deck-chair" arrangement of the Sb$_3$N$_6$Li core in [Sb$_3$(Ncy)$_4$(NMe$_2$)$_2$]Li (cy = cyclohexyl).[14] The mean Mg–N distance in the planar four-membered Mg$_2$N$_2$ ring of 2.262 Å is significantly longer than the corresponding distance of 2.06 Å in the hexagonal-prismatic [(thf)MgNPh]$_6$,[6a] presumably reflecting the higher coordination number (λ^6) of Mg^{2+} in **4**. The octahedral geometry about the magnesium center is significantly distorted by the formation of two chelate rings, (N1-Mg1-N2 67.33(15), N1*-Mg1-O1* 67.98(15)°). The geometry at the three-coordinate N2 atoms is exactly planar. The S–N and S–O distances are similar to those reported for dilithium diazasulfites.[13] Unlike the dilithium derivatives,[15] however, the magnesium diazasulfite **4** does not form colored radicals upon exposure to oxygen (ESR spectroscopy). In contrast to the reaction with SO$_2$, **4** is the only product formed when [(thf)MgNPh]$_6$ is treated with an excess of *t*BuNSO. On the other hand the reaction of [(thf)MgNPh]$_6$ with only six equivalents of SO$_2$ gives a 1:1 mixture of **2** and unconverted [(thf)MgNPh]$_6$.

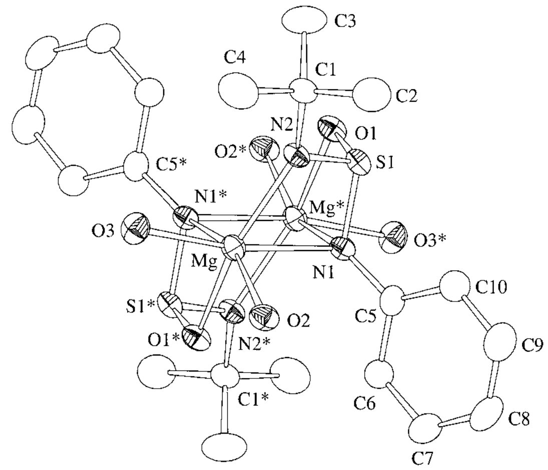


Figure 2. Molecular structure of **4**. For clarity, only the oxygen atoms of the THF molecules are shown, and H atoms are omitted. Displacement ellipsoids are plotted at the 40% probability level. Selected bond lengths [Å] and angles [°]: Mg1-O1* 2.065(4), Mg1-O2 2.117(4), Mg1-O3 2.156(4), Mg1-N1 2.295(4), Mg1-N1* 2.229(5), Mg1-N2 2.123(4), S1-N1 1.672(4), S1-N2 1.610(4), S1-O1 1.541(4); O1*-Mg1-N2 158.76(17), O2-Mg1-N1* 157.13(16), O3-Mg1-N1 170.09(17), O1-S1-N1 96.8(2), O1-S1-N2 110.6(2), N1-S1-N2 96.7(2). Symmetry transformation used to generate equivalent atoms marked with an asterisk: $-x+1, -y, -z+1$.

In summary, the reaction of the magnesium imide [(thf)MgNPh]$_6$ with sulfur dioxide provides the first example of the formal double insertion of two SO$_2$ molecules. The [PhN(SO$_2$)$_2$]$^{2-}$ ion **1** so generated is a potentially interesting multidentate ligand.

Experimental Section

All manipulations were carried out under anaerobic and anhydrous conditions.

2: Dry sulfur dioxide gas was bubbled into a stirred slurry of [(thf)MgNPh]$_6$[6c] (2.00 g, 1.78 mmol) in THF (60 mL) at 23 °C for 10 min. The reaction mixture became clear yellow and then cloudy. Removal of all volatile materials under vacuum and subsequent washing of the yellow residue with *n*-pentane (2 × 50 mL) yielded, after drying, pale yellow **2** (2.84 g, 1.50 mmol, 84 %); m.p. 140 °C (decomp.). Elemental analysis calcd for C$_{10}$H$_{13}$MgNO$_5$S$_2$: C 38.05, H 4.15, N 4.44; found: C 37.85, H 4.06, N 4.67; ^{1}H NMR (C$_6$D$_6$, 23 °C): δ = 7.81 (m, 2H, *o*-H), 7.03 (m, 2H, *m*-H), 6.86 (m, 1H, *p*-H), 3.84 (m, 4H, (CH$_2$)$_2$(C*H*$_2$)$_2$O), 1.25 (m, 4H, (C*H*$_2$)$_2$(CH$_2$)$_2$O); ^{13}C{^{1}H} NMR (C$_6$D$_6$, 23 °C): 139.3 (s, *ipso*-C), 129.4 (s, *o*-C), 129.2 (s, *m*-C), 126.7 (s, *p*-C), 68.8 (s, (CH$_2$)$_2$(*C*H$_2$)$_2$O), 25.2 (s, (*C*H$_2$)$_2$(CH$_2$)$_2$O).

4: A solution of *t*BuNSO[16] (0.50 g, 4.20 mmol) in THF (15 mL) was added slowly to a stirred slurry of [(thf)MgNPh]$_6$[6c] (0.79 g, 0.70 mmol) in THF

(45 mL) at 23 °C. The clear yellow reaction mixture was stirred for 4 h, and a precipitate formed. Removal of all volatile materials under vacuum and subsequent washing of the yellow residue with *n*-pentane (2 × 30 mL) yielded, after drying, powdery white **4** (1.32 g, 1.74 mmol, 83 %); m.p. 190 °C (decomp.). Elemental analysis calcd for $C_{18}H_{30}MgN_2O_3S$: C 57.07, H 7.98, N 7.40; found: C 57.35, H 7.77, N 7.59; ^{1}H NMR ([D$_8$]THF, 23 °C): 7.23 (br, 2 H, *o*-H), 6.86 (m, 2 H, *m*-H), 6.33 (m, 1 H, *p*-H), 3.58 (m, 8 H, $(CH_2)_2(CH_2)_2O$), 1.74 (m, 8 H, $(CH_2)_2(CH_2)_2O$), 1.34 (s, 9 H, $C(CH_3)_3$); $^{13}C\{^1H\}$ NMR ([D$_8$]THF, 23 °C): 154.0 (s, *ipso*-C), 128.4 (s, *o*-C), 115.0 (s, *m*-C), 96.8 (s, *p*-C), 67.9 (s, $(CH_2)_2(CH_2)_2O$), 52.4 (s, $C(CH_3)_3$), 34.3 (s, $C(CH_3)_3$), 26.4 (s, $(CH_2)_2(CH_2)_2O$).

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[9] a) Crystal data for **2**: $C_{10}H_{13}NO_5S_2Mg \cdot C_4H_8O$, $M_r = 387.75$, trigonal/hexagonal, space group $R\bar{1}$ (no. 148), $a = 26.871(4)$, $c = 13.506(10)$ Å, $V = 8446(6)$ Å^3, $Z = 18$, $\rho_{calcd} = 1.372$ g cm^{-3}, $\mu(Mo_{K\alpha}) = 0.345$ mm^{-1}, $\lambda(Mo_{K\alpha}) = 0.71069$ Å, $T = -103$ °C, $F(000) = 3672$. Data were collected on a Rigaku AFC6S diffractometer on a pale yellow needle (0.42 × 0.19 × 0.18 mm) coated with Paratone-8277 oil and mounted on a glass fiber by the $\omega/2\theta$ scan method. Of the 2725 reflections collected, 2551 were unique ($R_{int} = 0.221$), and 469 were observed $[I > 2\sigma(I)]$ and used to refine 101 parameters. The structure was solved by direct methods (SIR92), expanded with Fourier techniques (DIRDIF94) and refined by SHELXL97. The Mg and S atoms were refined anisotropically, and the rest of the non-hydrogen atoms were refined isotropically. The phenyl ring and THF molecules were included with constrained geometry. Hydrogen atoms were included but not refined. Refinement by full-matrix least-squares calculations converged at $R = 0.127$ and $R_w = 0.325$. Numerous attempts to obtain better quality crystals of **2** were unsuccessful. b) Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications no. CCDC-135289 (**2**) and -135290 (**4**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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[12] Crystal data for **4**: $C_{18}H_{30}N_2O_3SMg \cdot C_4H_8O$, $M_r = 450.92$, triclinic, space group $P\bar{1}$ (no. 2), $a = 11.8785(19)$, $b = 12.514(3)$, $c = 9.033(2)$ Å, $\alpha = 104.91(2)$, $\beta = 93.880(19)$, $\gamma = 71.223(16)$°, $V = 1228.3(5)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.219$ g cm^{-3}, $\mu(Mo_{K\alpha}) = 0.177$ mm^{-1}, $\lambda(Mo_{K\alpha}) = 0.71069$ Å, $T = -103$ °C, $F(000) = 488$. A colorless hexagonal prism (0.53 × 0.33 × 0.29 mm) was coated with Paratone-8277 oil and mounted on a glass fiber. Of the 4565 reflections collected, 4337 were unique ($R_{int} = 0.042$), and 2087 were observed $[I > 3\sigma(I)]$ and used to refine 271 parameters. The structure was solved by direct methods and expanded with Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included at geometrically idealized positions and were not refined. Refinement by full-matrix least-squares calculations converged at $R = 0.055$ and $R_w = 0.057$.[9b]

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Controllable Orientation of Helical Poly(L-glutamic acid) Rods through Macrodipole Interaction on Gold Surfaces and Vectorial Electron Transfer

Masazo Niwa,* Masa-aki Morikawa, and
Nobuyuki Higashi*

Helix orientation at interfaces is one of the key factors to fabricate biofunctional synthetic polymer systems that mimic natural polymers such as proteins. The orientation of segments in membrane proteins is known to govern functions such as molecular recognition and electrochemical communication, including electron transfer. In this context, there has been considerable interest in constructing perpendicularly oriented polypeptide monolayers on aqueous or solid substrates. It has been indicated that α helices prefer to lie flat on every possible interface.[1] Efforts have been made to orient α helices perpendicular to the surface of the water or solid substrates,[2–5] by incorporation of functional groups onto one terminus of polypeptide helices. Such groups under consideration include quaternary ammonium groups[6, 7] to interact with anionic templates, a crown ether moiety,[8–10] or a sulfur atom[11–14] to attach to a gold surface.

In this communication, we describe the reversible variation of the orientation of a disulfide-modified poly(L-glutamic acid) (PLGA-SS) α helix assemblies attached to a gold surface and their enhanced molecular packing based on the interaction of helix macroscopic dipoles ("macrodipoles"). We

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